Synthesis, reactivity and structural study of diastereomeric titanium complexes with amino acid derived N- and O-π donor ligands

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Dedicated to Ken Raymond on the occasion of his 60th birthday

Abstract

Two diastereomeric Ti(IV) complexes of the type $[Ti(Cl)(NMe_2)(-OCH_2CH(CH_2Ph)N(R)-)]_2$ (where R = ^iPr or *cyclo*-C_6H_{11}) have been synthesized by protonolysis of $TiCl(NMe_2)_3$ with the corresponding N-substituted amino alcohols. The chiral ligands were synthesized in a two-step procedure from L-phenylalanine ethyl ester. The complexes bridge through the amino alcohol oxygen atoms, and contain terminal chlorides. The remaining dimethylamide group can be replaced by a protonolysis reaction with 2,6-diisopropylphenol. The bulky disubstituted phenoxide ligand does not inhibit dimerization, and the amino alcohol oxygen bridged complex $[Ti(Cl)(O-2,6-^iPr_2-C_6H_3)(OCH_2CH(CH_2Ph)NR)]_2$ is obtained. The dimeric nature of the complexes was established by X-ray crystallography.
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1. Introduction

The organometallic chemistry of the early transition metals is dominated by complexes containing the cyclopentadienyl group and its derivatives [1]. There is a growing interest in alternative ligands, especially π-donor ligands such as amides [2–4], alkoxides [5], aryloxides [6–8], sulfonamides [9–12], and amidinates [13], since the dramatically different steric and electronic environments they provide can result in novel reactivity of the resulting complexes [14]. As one example, alkyne cyclotrimerization reactions have been observed for titanium aryloxide complexes, but are not known for metallocene complexes [15].

Since titanium complexes with amide and alkoxide ligands are known to carry out carbon–carbon bond forming reactions, chiral titanium complexes with amino alcohol ancillary ligands would be expected to carry out these reactions stereoselectively. In situ-generated titanium complexes with amino alcohol ancillary ligation do in fact stereospecifically catalyze, among others, the Diels–Alder reaction [16], and the alkylation of aldehydes [17], but isolable, well-characterized complexes of this sort have only been described recently [10].

In the present work we report the synthesis of two bidentate amino alcohol ligands derived from L-phenylalanine. The molecules contain substitutable groups to allow for further reactivity studies. Structural details of the resulting titanium complexes and their initial reaction chemistry are also reported.

2. Experimental

2.1. General details

All reagents were obtained from commercial suppliers and were purified by standard methods [18] or used as

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received. Solvents were degassed and distilled from sodium–benzophenone and stored under nitrogen. All air and/or moisture sensitive compounds were manipulated under an atmosphere of nitrogen using standard Schlenk techniques, or in a glove box (MBraun UNI-lab). Microanalyses were performed by Desert Analytics (Tucson, AZ). Mass spectra were obtained at the Mass Spectrometry Facility, University of California, Riverside, CA. All NMR spectra were recorded at ambient temperature on a Brüker Avance 400 spectrometer. Carbon assignments were made using DEPT experiments. Melting points were taken on a Meltemp melting apparatus and are uncorrected. Polarimetry was carried out using a Perkin–Elmer 141 instrument with a sodium lamp (589 nm). X-ray crystal structures were determined at the W.M. Keck Foundation Center for Molecular Structure, California State University Fullerton.

2.2. Preparations

2.2.1. Ethyl (2S)-2-(cyclohexylamino)-3-phenylpropanoate (1)

L-Phenylalanine ethyl ester (3.7 g, 19 mmol) was dissolved in THF (100 ml) under nitrogen. $NaBH(OAc)_3$ (17 g, 80 mmol), cyclohexanone (4.5 ml, 43 mmol) and glacial acetic acid (2.6 ml, 44 mmol) were added and the mixture was stirred under nitrogen for 2 days. The reaction was quenched with acetic acid (10% in methanol, 60 ml) and the solvent was removed in vacuo. The remaining thick oil was dissolved in water, acidified with a minimum amount of hydrochloric acid, and washed with ether. The aqueous solution was brought to pH 10 with sodium hydroxide pellets and extracted with fresh ether. The ether was washed with sodium bicarbonate (1 M, 2 × 150 ml) and brine (150 ml), and dried ($MgSO_4$). The solvent was removed in vacuo leaving a pale yellow oil (4.5 g, 16 mmol, 84% yield). ^1H NMR (400 mHz, CDCl$_3$): δ = 7.19–7.28 (m, 5H, Ph); 4.1 (q, $J = 7.1$ Hz, 2H, CH$_2$CH$_3$); 3.7 (m, 1H, CH); 2.9 (m, 2H, CH$_2$Ph); 2.4 (m, 1H, Cy–CH); 1.14–1.71 (br m, 10 H, Cy); 1.14 (t, $J = 7.0$ Hz, CH$_2$CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 175.4 (C=O), 137.6 (aryl), 129.3 (aryl CH), 128.5 (aryl CH), 126.7 (aryl CH), 60.6 (CH$_2$), 60.4 (CH), 55.3 (CH), 40.4 (CH$_2$), 34.3 (CH$_2$), 32.8 (CH$_2$), 26.2 (CH$_2$), 25.1 (CH$_2$), 24.8 (CH$_2$), 14.3 (CH$_3$). b.p. 122–123 °C (<1 mm Hg). MS (DEI, 70 eV) m/z(%): 276(100)[MH$^+$]. Anal. Calc. for C$_{17}$H$_{25}$NO$_2$: C, 74.14; H, 9.15; N, 5.09. Found: C, 73.98; H, 8.99; N, 5.28%.

2.2.2. Ethyl (2S)-2-[(isopropyl)amino]-3-phenylpropanoate (2)

This compound was prepared analogously to 1 from L-phenylalanine ethyl ester (3.5 g, 18 mmol), NaBH(OAc)$_3$ (5.8 g, 16 mmol), acetone (1.3 ml, 16 mmol) yielding the desired compound as a pale yellow oil (3.9 g, 16 mmol, 89%). ^1H NMR (400 mHz, CDCl): δ = 7.15–7.28 (m, 5H, Ph); 4.06 (q, $J = 7.2$ Hz, 2H, CH$_2$CH$_3$); 3.60 (dd, $J = 6.4$, 7.6 Hz, 1H, CHC=O); 2.8–3.0 (m, 2H, CH$_2$Ph); 2.75 (m, 1H, CHMe$_2$); 1.12 (t, $J = 7.2$ Hz, 3H, CH$_2$CH$_3$); 1.04 (d, $J = 6.4$ Hz, 3H, CH$_3$); 0.99 (d, $J = 6.0$ Hz, 3H, CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 175.5 (C=O); 137.8 (aryl), 129.6 (aryl CH); 128.7 (aryl CH); 127.0 (aryl CH); 61.1 (CH); 60.8 (CH$_2$); 47.4 (CH); 40.7 (CH$_2$); 24.1 (CH$_3$); 22.4 (CH$_3$); 14.5 (CH$_3$). b.p. 105–110 °C (<1 mm Hg). $[\alpha]_D^{20}$ ($c = 0.334$ g^{-1} 10.0 ml EtOAc): 11.0°. MS (DEI, 70 eV) m/z(%): 236(100)[MH$^+$]. Anal. Calc. for C$_{14}$H$_{21}$NO$_2$: C, 71.46; H, 8.99; N, 5.95. Found: C, 71.44; H, 8.88; N, 5.98%.

2.2.3. (2S)-2-(cyclohexylamino)-3-phenylpropan-1-ol (H$_2$L1)

Ester 1 (4.8 g, 17 mmol) was dissolved in anhydrous THF (100 ml) under nitrogen. Lithium aluminum hydride (4.0 g, 87 mmol) was added slowly to the stirring solution. The solution was kept at 75 °C in an oil bath under nitrogen overnight. The solution was diluted with ether (200 ml) and quenched with water (4 ml), sodium hydroxide (15%, 4 ml), and water (12 ml). The white precipitate that formed was removed by filtration, and the resulting solution was washed with sodium bicarbonate (1 M, 2 × 200 ml) and brine (200 ml). The organic layer was dried ($MgSO_4$), filtered, and the solvent was removed in vacuo to yield a white powder (2.7 g, 12 mol, 68%). The compound can be recrystallized from hexanes. ^1H NMR (400 MHz, CDCl$_3$): δ = 7.09–7.33 (m 5H, Ph); 3.55 (dd, $J = 10.4$, 4.0 Hz, 1H, CH$_a$H$_b$OH); 3.24 (dd, $J = 10.8$, 5.6 Hz, 1H, CH$_a$H$_b$OH); 3.03 (m, 1H, CH); 2.74 (m, 2H, CH$_2$Ph); 2.46 (m, 1H, Cy–CH); 2.2 (br, s, 2H, NH, OH); 1.88 (m, 1H, Cy); 1.5–1.7 (m, 4H, Cy); 0.9–1.3 (m, 5H, Cy). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 139.0 (aryl), 129.6 (aryl CH), 128.9 (aryl CH), 126.8 (aryl CH), 63.4 (CH$_2$), 57.2 (CH), 54.1 (CH), 39.1 (CH$_2$), 34.6 (CH$_2$), 34.3 (CH$_2$), 26.4 (CH$_2$), 25.4 (CH$_2$), 25.3 (CH$_2$). M.p. 65.0–66.1 °C. $[\alpha]_D^{20}$ ($c = 0.0333$ g^{-1} 10 ml EtOAc): +1.28°. MS (DEI, 70 ev) m/z(%): 234(72)[MH$^+$]. Anal. Calc. for C$_{15}$H$_{23}$NO: C, 77.21; H, 9.93; N, 6.00. Found: C, 77.17; H, 10.26; N, 6.07%.

2.2.4. (2S)-2-[(isopropyl)amino]-3-phenylpropan-1-ol (H$_2$L2)

This compound was prepared analogously to H$_2$L1 from ester 2 (7.72 g, 40 mmol) and lithium aluminum hydride (6 g, 130 mmol) yielding the desired compound as a white solid (4.4 g, 23 mmol, 58%). ^1H NMR (400 MHz, CDCl$_3$): δ = 7.17–7.33 (m, 5H, Ph); 3.54 (m, 1H); 3.23 (m, 1H); 2.86 (m, 1H); 2.71–2.76 (m, 3H); 1.03 (d, $J = 6.4$ Hz, 3H, CH$_3$); 0.98 (d, $J = 6.0$ Hz, 3H, CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 139.0 (aryl), 129.6 (aryl CH), 128.9 (aryl CH), 126.7 (aryl CH), 63.5 (CH$_2$), 57.7 (CH), 46.3 (CH), 39.0 (CH$_2$), 23.9 (CH$_3$), 23.8 (CH$_3$).

m.p. 38.8–59.5 °C. $[\alpha]_D^{20}$ ($c = 0.0333$ g^{-1} 10 ml EtOAc): +4.40°. MS (DEI, 70 ev)) m/z (%): 194(100) [MH$^+$]. *Anal*. Calc. for $C_{12}H_{19}NO$: C, 74.57; H, 9.91; N, 7.25. Found: C, 74.30; H, 9.83; N, 7.13%.

2.2.5. [Ti(Cl)(NMe₂)(L1)]₂ (3a)

To a solution of TiCl(NMe₂)₃ [19] (0.504 g, 2.34 mmol) dissolved in ether (5 ml) was added a solution of **H₂L1** (0.548 g, 2.34 mmol) dissolved in ether (5 ml). The solution rapidly turned dark red. The reaction mixture was stirred overnight, and the solvent was removed in vacuo. The complex was isolated as a red microcrystalline powder in low yield (~45%). ^{1}H NMR (400 MHz, C_6D_6): $\delta = 7.5$ (m, 2H); 7.3 (m, 2H); 7.1 (m, 1H); 5.2 (br d, 1H); 4.9 (br m, 1H); 4.6 (br m, 1H); 3.6 (br m, 2H); 3.2 (s, 6H); 3.1 (br m, 1H); 2.6 (br m, 1H); 1.9 (br m, 3H); 1.3–1.5 (br m, 6H, NMe₂). ^{13}C NMR (100 MHz, C_6D_6): $\delta = 140.0$ (aryl); 130.5 (aryl CH); 129.0 (aryl CH); 126.9 (aryl CH); 82.9 (CH₂); 70.1 (CH); 64.1 (CH); 47.7 (CH₃); 42.6 (CH₂); 34.6 (CH₂); 34.0 (CH₂); 27.7 (CH₂); 27.1 (CH₂); 26.6 (CH₂). m.p. 130° (dec). *Anal*. Calc. for $C_{34}H_{54}Cl_2N_4O_2Ti_2$: C, 56.92; H, 7.59; N, 7.81; Found: C, 56.39; H, 7.68; N, 7.46%.

2.2.6. [Ti(Cl)(NMe₂)(L2)]₂ (3b)

Complex **3b** was prepared similarly from TiCl(NMe₂)₃ [19] (0.81 g, 3.7 mmol) and **H₂L2** (0.73 g, 3.7 mmol). The complex was isolated as a red microcrystalline powder in low yield (~40%). ^{1}H NMR (400 MHz, C_6D_6): $\delta = 7.6$ (m, 2H); 7.4 (m, 2H); 7.1 (m, 1H); 5.2–5.3 (m, 2H); 4.5 (m, 1H); 3.5 (br m, 1H); 3.3 (m, 1H); 3.1 (s, 6H; NMe₂); 3.0 (br m, 1H); 1.49 (d, $J = 6.8$ Hz, 3H, CH₃); 1.29 (d, $J = 6.8$ Hz, 3H, CH₃). ^{13}C NMR (100 MHz, C_6D_6): $\delta = 140.0$ (aryl); 130.4 (aryl CH); 129.0 (aryl CH); 126.8 (aryl CH); 82.8 (CH₂); 69.5 (CH); 54.7; 48.6; 47.6; 42.5; 23.6 (CH₃); 22.7 (CH₃). M.p. 125–128 °C. *Anal*. Calc. for $C_{28}H_{46}Cl_2N_4O_2Ti_2$: C, 52.77; H, 7.27; N, 8.79. Found: C, 52.74; H, 7.58; N, 8.51%.

2.2.7. [Ti(Cl)(OAr′)(L2)]₂ (4b)

To a solution of [Ti(Cl)(NMe₂)(L2)]₂ (**3b**, 1.27 g, 3.79 mmol) in ether (10 ml) was added 2,6-diisopropylphenol (HOAr′, 0.702 ml, 3.78 mmol). The reaction mixture was stirred overnight, and the solvent was removed in vacuo. The complex was isolated as a red–orange powder in low yield (~40%). Proton and carbon NMR spectra were complex m.p. 88 °C (dec). *Anal*. Calc. for $C_{48}H_{68}Cl_2N_2O_4Ti_2$: C, 63.79; H, 7.58; N, 3.10. Found: C, 63.39; H, 7.55; N, 3.02%.

2.3. Chiral shift studies

H₂L1 (0.015 g, 0.064 mmol) or **H₂L2** (0.015 g, 0.078 mmol) was dissolved in CDCl₃ (ca. 1 ml) and examined by ^{1}H NMR spectroscopy. (S)-(+)-2,2,2-Trifluoro-1-(9-anthryl)ethanol (1 equiv.) was added to the NMR tube,

and the solution was reexamined. Additional shift reagent (2 equiv. total) was added, and the solution was reexamined.

2.4. X-ray crystal structure determinations

2.4.1. [Ti(Cl)(NMe₂)(L1)]₂ (3a)

Suitable crystals were obtained by slow evaporation of a saturated ether solution. Data were collected from a single crystal at −30 °C on a SMART© CCD detector system using graphite monochromated Mo Kα radiation. An entire hemisphere of data was collected in multirun mode with ω as the rotation axis. Detector-to-sample distance was 5.25 cm, the detector 2θ angle was 28°, rotation width was 0.3°, frame size was 512×512 pixels, and data collection time per frame was 60 s. The total number of frames collected was 1868, and the total time for data collection was ~36 h. SMART v5.618© was used for collecting data frames, indexing of reflections and determination of lattice parameters. SAINT+ v6.02© was used for integration of the intensity of reflections. SHELXTL v6.10© was used for data reduction, space group determination, structure determination, structure refinement and structure reporting.

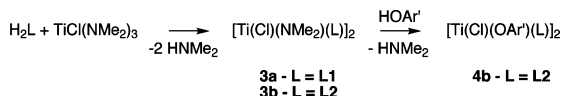#### 2.4.2. X-ray crystal structure of [Ti(Cl)(OAr′)(L2)]₂ (4b)

Suitable crystals were obtained by slow evaporation of a saturated ether solution. Data were collected from a single crystal at −30 °C on a SMART© CCD detector system using graphite monochromated Mo Kα radiation using the same protocol outlined in Section 2.4.1.

3. Results and discussion

The preparation of *N*-alkyl derivatives of phenylalanine ethyl ester by reductive amination was investigated using a variety of common reducing agents. Initial attempts using sodium cyanoborohydride [20] proceeded slowly, and in relatively low yields, but when sodium triacetoxyborohydride [21] is used, the synthesis is straightforward and gives good yields. Reduction of the ester function with lithium aluminum hydride proceeds to give the desired solid ligands **H₂L1** and **H₂L2** in moderate yield (Scheme 1). The reduction products were examined by polarimetry (both **H₂L1**
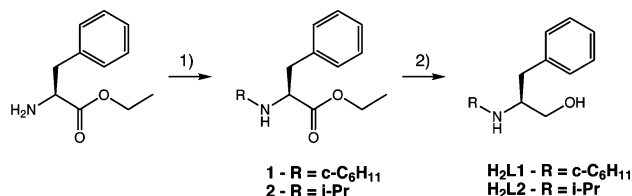
Scheme 1. The synthesis of ligands **H₂L1** and **H₂L2**. Step 1: NaBH(OAc)₃, cyclohexanone or acetone. Step 2: LiAlH₄.

H$_2$L + TiCl(NMe$_2$)$_3$ $\xrightarrow[\text{-2 HNMe}_2]{}$ [Ti(Cl)(NMe$_2$)(L)]$_2$ $\xrightarrow[\text{- HNMe}_2]{\text{HOAr'}}$ [Ti(Cl)(OAr')(L)]$_2$

3a - L = L1
3b - L = L2   **4b** - L = L2

Scheme 2. Synthesis of titanium complexes. Ar′ = *O*-2,6-^{i}Pr$_2$C$_6$H$_3$.

(+1.28°) and **H$_2$L2** (+4.40°) are chiral). In order to ensure that partial racemization had not occurred, chiral shift NMR studies were undertaken. Addition of 1 or 2 equiv. of *S*-(+)-2,2,2-Trifluoro-1-(9-anthryl)ethanol [22] to either **H$_2$L1** or **H$_2$L2** in chloroform show a shifting of the resonances corresponding to the ligand protons, but a second set of diastereomeric resonances is not observed.

Protonolysis of TiCl(NMe$_2$)$_3$ [19] with either **H$_2$L1** or **H$_2$L2** proceeds with loss of 2 equiv. of HNMe$_2$ to give the desired amido–alkoxide complexes **3a** and **3b** (Scheme 2). Although the reaction to form **3a** or **3b** appears quantitative by NMR spectroscopy, the complexes are isolated in low yield due their high solubility when impure. The NMR spectrum of **3a** is complex in the aliphatic region, but there are three distinct signals between 4.5 and 5.5 ppm, each integrating to one proton. The NMR signals are somewhat broad, consistent with some degree of aggregation in solution. Variable temperature NMR spectroscopy (ambient down to −60 °C in toluene-d$_8$) shows no significant changes. The NMR spectrum of **3b** is sharp and well resolved, with the isopropyl group appearing as two sets of doublets at 1.49 and 1.29 ppm, and there are again three distinct signals between 4.5 and 5.5 ppm.

Both complexes **3a** and **3b** are dimeric in nature; an ORTEP [23] and partial atom numbering scheme of **3a** is shown in Fig. 1 [24]. Table 1 lists selected bond distances and angles for the metal coordination environment. Crystallographic data collection parameters and refinement statistics are listed in Table 2. There are two molecules of **3a** in the asymmetric unit; only one is shown for clarity. The two molecules are not equivalent,
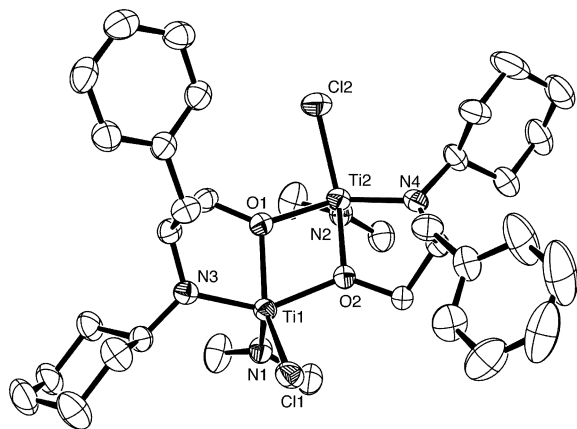

Fig. 1. ORTEP and partial atom numbering scheme for one of the two independent molecules of complex **3a**. Ellipsoids are shown with 30% probability. Hydrogen atoms are omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for **3a**

Bond lengths			
Ti1–O1	2.027(5)	Ti2–O2	2.025(5)
Ti1–O2	1.992(5)	Ti2–O1	1.997(5)
Ti1–N3	1.896(5)	Ti2–N4	1.886(5)
Ti1–Cl	2.303(7)	Ti2–Cl2	2.300(4)
Ti1–N1	1.861(4)	Ti2–N2	1.847(5)
Bond angles			
N1–Ti1–N3	103.6(2)	N2–Ti2–N4	104.5(2)
N1–Ti1–O2	103.3(2)	N2–Ti2–O1	106.28(18)
N3–Ti1–O2	144.02(14)	N4–Ti2–O1	140.55(17)
N1–Ti1–O1	111.3(2)	N2–Ti2–O2	106.4(2)
N3–Ti1–O1	77.9(2)	N4–Ti2–O2	77.8(3)
O2–Ti1–O1	70.3(2)	O1–Ti2–O2	70.22(18)
N1–Ti1–Cl1	108.54(18)	N2–Ti2–Cl2	105.4(2)
N3–Ti1–Cl1	101.39(15)	N4–Ti2–Cl2	102.0(2)
O2–Ti1–Cl1	92.21(15)	O1–Ti2–Cl2	93.0(2)
O1–Ti1–Cl1	139.14(11)	O2–Ti2–Cl2	147.12(11)
Ti1–O1–Ti2	107.9(2)	Ti1–O2–Ti2	108.2(2)

Table 2
Crystallographic data collection parameters and refinement statistics for **3a** and **4b**

	3a	**4b**
Empirical formula	C$_{34}$H$_{54}$Cl$_2$N$_4$O$_2$Ti$_2$	C$_{48}$H$_{68}$Cl$_2$N$_2$O$_4$Ti$_2$
Formula Weight	1436.35	903.74
Color, habit	red, crystal	red, crystal
Approximately crystal size (mm)	0.2 × 0.1 × 0.4	0.2 × 0.2 × 0.3
Crystal system	monoclinic	monoclinic
Space group	*P*2$_1$ (No. 4)	*P*2$_1$ (No. 4)
a (Å)	12.1682(12)	14.2116(33)
b (Å)	25.3992(25)	10.4336(29)
c (Å)	13.3201(13)	16.8731(44)
β (°)	111.054(4)	99.689(10)
V (Å^3)	3843(19)	2466(25)
Z	4	2
T (°C)	243(2)	243(2)
D$_{calc}$ (g cm^{-3})	1.241	1.217
F(000)	1520	960
Radiation	Mo Kα (0.71073)	Mo Kα (0.71073)
μ (mm^{-1})	0.587	0.474
Scan mode	*ω*	*ω*
θ Range (°)	1.60–23.35	1.22–26.61
Index ranges	−13 = *h* = 13	−17 = *h* = 4
	−28 = *k* = 28	−12 = *k* = 7
	−14 = *l* = 13	−18 = *l* = 21
Total number of reflections	25 312	8339
Number of unique reflections	11 101	6752
Number reflections with *I* > 2*σ*(*I*)	8950	5840
R$_{int}$	0.0511	0.1518
Data/restraints/parameters	11 101/1/822	6752/1/546
Final *R* indicies [*I* > 2*σ*(*I*)]	0.0606/0.0428	0.0851/0.0704
Weighted *R* [*I* > 2*σ*(*I*)]	0.0887/0.0822	0.1985/0.1778
Goodness-of-fit	1.033	1.173
Residual density (e Å^{-3})	−0.17, 0.20	−0.82, 0.46

with an rms fit of 4.314 Å for all atoms, and are related by a rotation of 175.79°. The two independent molecules differ mainly in the relative position of the cyclohexyl group on the **L1** ligand. The ligand binds to titanium to form a five-membered metallocycle, and the amino alcohol oxygen bridges the two titanium centers. Each titanium has a highly distorted trigonal bipyramidal coordination environment. This structural motif has been observed previously in amido–alkoxide complexes of titanium [10,25]. The two titanium–oxygen bond distances differ, with the Ti–O_{axial} (Ti1–O2 and Ti2–O1) bonds shorter by approximately 0.03 Å than the Ti–O_{eq} (Ti1–O2 and Ti2–O1) bonds. The complex also contains a terminal chloride and dimethylamide ligand. One of the two molecules contains a rotationally disordered dimethylamide group. Each independent molecule is nearly twofold symmetric, with the rotation axis perpendicular to the Ti1–O1–Ti2–O2 linkage. The remaining bond distances and angles are unremarkable.

Complexes **3a** and **3b** are expected to be good starting materials for a variety of inorganic and organometallic complexes due to the reactive dimethylamide and chloride groups. Importantly, the groups have orthogonal reactivity; the dimethylamide group should react with protic reagents while the chloride can be displaced by metathesis reactions. The initial reaction chemistry of **3a** and **3b** was examined with a variety of bulky substituted phenols. The nucleophilic substitution chemistry of these complexes will be reported subsequently.

The products of the protonolysis reactions with a number of 2,6-disubstituted phenols were intractable oils with complicated NMR spectra. Complex **3a** reacts cleanly with 2,6-diisopropylphenol to give a well-resolved set of NMR signals. A doubling of peaks is observed in the NMR spectrum of the product (each of the well-resolved signals between 4.5 and 5.5 ppm splits into two peaks), but efforts to obtain this complex as a

Table 3
Selected bond lengths (Å) and angles (°) for **4b**

Bond lengths			
Ti1–O1	1.777(8)	Ti2–O4	1.783(8)
Ti1–N2	1.898(12)	Ti2–N5	1.912(12)
Ti1–O2	1.966(10)	Ti2–O3	1.984(9)
Ti1–O3	2.045(10)	Ti2–O2	2.046(10)
Ti1–Cl1	2.269(9)	Ti2–Cl2	2.265(9)
Bond angles			
O1–Ti1–N2	101.1(4)	O4–Ti2–N5	104.5(4)
O1–Ti1–O2	137.4(3)	O4–Ti2–O3	138.4(3)
N2–Ti1–O2	78.5(4)	N5–Ti2–O3	78.5(4)
O1–Ti1–O3	96.1(4)	O4–Ti2–O2	93.7(4)
N2–Ti1–O3	146.5(3)	N5–Ti2–O2	146.2(3)
O2–Ti1–O3	69.5(5)	O3–Ti2–O2	69.1(5)
O1–Ti1–Cl1	106.6(4)	O4–Ti2–Cl2	106.5(4)
N2–Ti1–Cl1	104.7(3)	N5–Ti2–Cl2	104.3(3)
O2–Ti1–Cl1	114.7(4)	O3–Ti2–Cl2	113.0(4)
O3–Ti1–Cl1	97.4(4)	O2–Ti2–Cl2	97.4(4)
Ti1–O2–Ti2	110.7(5)	Ti1–O3–Ti2	109.9(5)

crystalline solid have thus far been unsuccessful. Complex **3b** also reacts with 2,6-diisopropylphenol, but the resulting NMR spectrum of **4b** is extremely complicated, suggesting aggregation or fluxional processes in solution.

To determine if the bulkier aryloxide ligand provided a monomeric structure, complex **4b** was examined by X-ray crystallography, but this complex was also found to be dimeric. An ORTEP [23] and partial atom numbering scheme of **4b** is shown in Fig. 2. Table 3 lists selected bond distances and angles for the metal coordination environment, and crystallographic data collection parameters and refinement statistics are listed in Table 2. The structure contains one molecule in the asymmetric unit, and the isopropyl group on N5 is disordered, occupying two possible positions in the crystal lattice. Again, the amino alcohol ligand binds to titanium to form a five-membered metallocycle, and the amino alcohol oxygen bridges the two titanium centers. Each titanium has a highly distorted trigonal bipyramidal geometry, but in this structure the Ti–O_{axial} (Ti1–O3 and Ti2–O2) bonds are longer by approximately 0.07 Å than the Ti–O_{eq} (Ti1–O2 and Ti2–O3) bonds. The Ti–OAr′ bond distances (Ti1–O1 and Ti2–O4) are significantly shorter at about 1.78 Å. The two halves of the titanium dimer are nearly related by inversion symmetry, although the phenyl rings on the two **L2** ligands reside on the same face of the molecule. Otherwise, the metrical parameters are unexceptional compared with other Ti(IV) complexes.

4. Summary and conclusions

We have prepared three new diastereomeric titanium(IV) complexes with chiral amino alcohol ligands
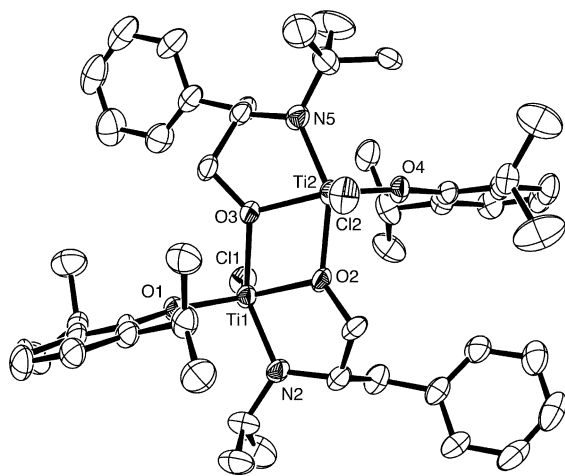

Fig. 2. ORTEP and partial atom numbering scheme of complex **4b**. Ellipsoids are shown with 30% probability. Hydrogen atoms are omitted for clarity.

derived from L-phenylalanine. The complexes are dimeric in the solid state, bridging through the oxygen atoms. The dimethylamide ligand on the complex can be replaced with an aryloxide ligand by protonolysis, again resulting in a dimeric complex bridging through the amino alcohol oxygen.

5. Supplementary information

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 191997 and 191998. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336-033; e-mail: deposit@ccdc.cam.a-c.uk or www: http://www.ccdc.cam.ac.uk).

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